CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION,
CANOGA PARK, CALIFORNIA 91304

Chlorine Trifluoride Oxide. VII. The Difluorooxychloronium(V) Cation, ClF_2O^+. Vibrational Spectrum and Force Constants

BY KARL O. CHRISTE,* E. C. CURTIS, AND CARL J. SCHACK

Received September 8, 1971

The vibrational spectra have been recorded for the solid 1:1 adducts, $ClF_3O \cdot BF_3$, $ClF_3O \cdot AsF_5$, and $ClF_3O \cdot SbF_5$, and for $ClF_3O \cdot BF_3$ in HF solution. These spectra are entirely consistent with the ionic structures, $ClF_2O^+BF_4^-$, $ClF_2O^+AsF_6^-$, and $ClF_2O^+SbF_6^-$, respectively. Six fundamental vibrations have been observed for ClF_2O^+, consistent with symmetry C_s. The structure of ClF_2O^+ can be derived from a tetrahedron with the chlorine atom located at the center and with two fluorine atoms, one oxygen atom, and one free electron pair at the four corners. The vibrational spectrum and structure of ClF_2O^+ closely resemble those of isoelectronic SOF_2. An assignment of the fundamental vibrations is proposed for ClF_2O^+, and a modified valence force field has been calculated. A mainly covalent bond model is considered most likely for ClF_2O^+.

Introduction

Chlorine trifluoride oxide possesses amphoteric character and forms adducts with BF_3, AsF_5, SbF_5, and SiF_4.[1] In this paper, we report the vibrational spectra and a structural study of some of these adducts.

Experimental Section

The preparation of the ClF_2O^+ containing salts, the apparatus, handling procedures, and the techniques used for recording the vibrational spectra have previously been described.[1-3]

Results and Discussion

Vibrational Spectra.—Figures 1 and 2 show the infrared and Raman spectra of solid $ClF_2O^+BF_4^-$ and $ClF_2O^+AsF_6^-$, respectively. Figure 3 shows the Raman spectrum of $ClF_2O^+BF_4^-$ in HF solution. The observed frequencies are listed in Table I and are compared with those reported for isoelectronic SOF_2.[4] The vibrational spectrum of the 1:1.2 ClF_3O–SbF_5 adduct was also recorded. The infrared spectrum of a dry powder sample showed, in the range 4000–400 cm^{-1}, absorptions at the following wave numbers: 1339 sh, w, 1331 s, 1319 m, 740 s, 710 vs, 658 vs, 600 s, 559 mw, 510 ms, and 401 mw. The Raman spectrum of the solid showed bands at the following wave numbers (relative intensity): 1329 (4), 1316 (2), 741 (5), 686 (1), 670 (5), 637 (10), 590 (1), 554 (2), 504 (3), 397 (3), 377 (0+), and 282 br (4).

The adducts between ClF_3O and Lewis acids could be either ionic or fluorine bridged coordination complexes. The simplicity of the observed spectra, the shift of the Cl═O stretching vibration to higher frequencies when compared to that in ClF_3O,[5] and the occurrence of all bands characteristic for the corresponding anion suggest that solid $ClF_3O \cdot AsF_5$ and $ClF_3O \cdot BF_3$ have the ionic structures $ClF_2O^+AsF_6^-$ and $ClF_2O^+BF_4^-$, respectively. The Raman spectrum of $ClF_2O^+BF_4^-$ in HF solution closely resembles that of the solid, indicating the presence of discrete ions in both the solid state and HF solution. Table I shows the observed vibrational spectra, together with their assignment. The vibrational spectra of AsF_6^- and BF_4^-, respectively, are well known and hence will be discussed first.

An octahedral ion, such as AsF_6^-, has O_h symmetry. The six normal modes of vibration are classified as $A_{1g} + E_g + 2F_{1u} + F_{2g} + F_{2u}$. Of these, only the two F_{1u} modes will be infrared active, while only the A_{1g} E_g, and F_{2g} modes will be Raman active, assuming that the selection rules are valid and that the octahedron is not distorted. The remaining F_{2u} mode is inactive in both the infrared and Raman spectrum. For $ClF_3O \cdot AsF_5$, all five active modes belonging to AsF_6^- were observed, the observed frequencies and intensities being similar to those of other AsF_6^- containing complexes, such as $ClF_2^+AsF_6^-$,[6] $NF_4^+AsF_6^-$,[7] $NF_2O^+AsF_6^-$,[8] $IF_6^+AsF_6^-$,[9] and $ClO_2^+AsF_6^-$.[10] Several deviations from the selection rules for O_h were observed. The $\nu_2(E_g)$ mode should be Raman active only but was also observed in the infrared spectrum. Furthermore, the two triply degenerate modes, ν_3 and ν_4, in species F_{1u} show shoulders in the infrared spectrum. This breakdown of the selection rules has also been observed for the infrared spectra of most of the other AsF_6^- containing salts.[6-10] It could be due to site symmetry lowering, slight distortion of the AsF_6^- octahedron, or weak fluorine bridges.

A tetrahedral ion, such as BF_4^-, has T_d symmetry. The four normal modes of vibration are classified as $A_1 + E + 2F_2$. Of these, all four modes are expected to be Raman active, whereas only the two F_2 modes should be infrared active. However, crystal-field effects or slight distortion of the BF_4^- tetrahedron can result in the A_1 mode also becoming infrared active. For $ClF_3O \cdot BF_3$, all four modes belonging to BF_4^- were observed and assigned by analogy with the known spectra of $K^+BF_4^-$,[11-14] $ClF_2^+BF_4^-$,[6] $ClO_2^+BF_4^-$,[10] and $FCl_2^+BF_4^-$.[15,16]

---

(1) K. O. Christe, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, **11**, 2205 (1972).

(2) K. O. Christe and E. C. Curtis, *ibid.*, **11**, 2209 (1972).

(3) K. O. Christe, *ibid.*, **9**, 2801 (1970).

(4) E. L. Pace and H. V. Samuelson, *J. Chem. Phys.*, **44**, 3682 (1966).

(5) K. O. Christe and E. C. Curtis, *Inorg. Chem.*, **11**, 2196 (1972).

(6) K. O. Christe and W. Sawodny, *ibid.*, **6**, 313 (1967).

(7) K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, *ibid.*, **6**, 533 (1967).

(8) K. O. Christe and W. Maya, *ibid.*, **8**, 1253 (1969).

(9) K. O. Christe and W. Sawodny, *ibid.*, **6**, 1783 (1967).

(10) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *ibid.*, **8**, 2489 (1969).

(11) J. Goubeau and W. Bues, *Z. Anorg. Allg. Chem.*, **268**, 221 (1952).

(12) N. N. Greenwood, *J. Chem. Soc.*, 3811 (1959).

(13) J. A. A. Ketalaar and R. L. Fulton, *Z. Elektrochem.*, **64**, 641 (1960).

(14) H. A. Bonadeo and E. Silberman, *Spectrochim. Acta, Part A*, **26**, 2337 (1970).

(15) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **8**, 212 (1969).

(16) R. J. Gillespie and M. J. Morton, *ibid.*, **9**, 811 (1970).

TABLE I

VIBRATIONAL SPECTRA OF ClF_2O^+ SALTS COMPARED WITH THAT OF SOF_2

Observed frequencies, cm^{-1}, and relative intensities								Assignment		
$ClF_2O^+BF_4^-$			$ClF_2O^+AsF_6^-$		SOF_2[a]					
Raman										
HF soln	Solid	Ir	Raman	Ir	Raman (gas)	Raman (liq)	Ir (gas)	OXF_2 (C_s)	AsF_6^- (O_h)	BF_4^- (T_d)
1333 (3.5) 1323 sh } P	1333 (4) 1321 sh (2) }	1334 s 1322 m }	1333 (2) 1320 (1) }	1331 ms 1319 mw }	1339 1329 } (10)	1308 (10)	1341 1331 } s	$\nu_1(A')$		
		1295 m								$\nu_1 + \nu_4(F_2)$
	1020 (0+), br	990–1150 vs								$\nu_3(F_2)$
				820 sh					$\nu_1 + \nu_6(F_{2u})$	
771 (2), P	771 (3)	772 w								$\nu_1(A_1)$
741 (10), P	731 (10)	734 m	757 br (3)	750 br, s	808 (10)	804 (6)	808 s	$\nu_2(A')$		
710 sh, dp	695 (5)	694 s	696 (1)	695 vs	747 (4)	716 (6)	747 vs	$\nu_5(A'')$		
				695 vs					$\nu_3(F_{1u})$	
			674 (10)	675 sh, w					$\nu_1(A_{1g})$	
			563 (3)	561 ms					$\nu_2(E_g)$	
	530 sh (1)	532 w								$\nu_4(F_2)B^{10}$
	519 (2)	521 sh								$\nu_4(F_2)B^{11}$
512 (2.5), P	513 (3)	514 s	511 (2)	509 ms	530 (8)	528 (8)	530 w	$\nu_3(A')$		
402 (1.9)	404 (4)	405 m	406 (2)	407 sh	390 (4)	399 (7)	393 w	$\nu_6(A'')$		
				388 s					$\nu_4(F_{1u})$	
383 (1)	384 (2)	383 m	378 sh (1)	378 sh	390 (4)	380 (5)	378 vw	$\nu_4(A')$		
			371 (4)						$\nu_5(F_{2g})$	
355 (0+)	356 (1)	356 mw								$\nu_2(E)$

[a] See ref 4.

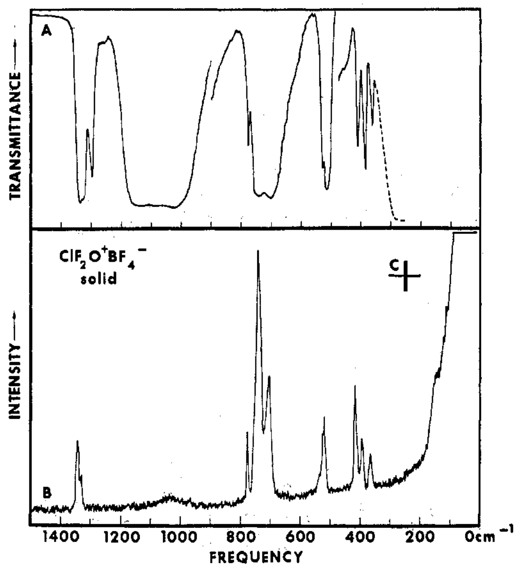

Figure 1.—Vibrational spectrum of solid $ClF_2O^+BF_4^-$: (A) infrared spectrum recorded as a AgCl disk; (B) Raman spectrum, exciting line 4880 Å. C indicates spectral slit width.

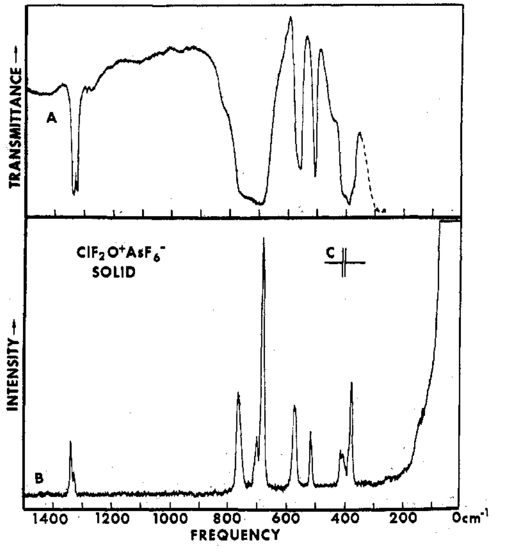

Figure 2.—Vibrational spectrum of solid $ClF_2O^+AsF_6^-$.

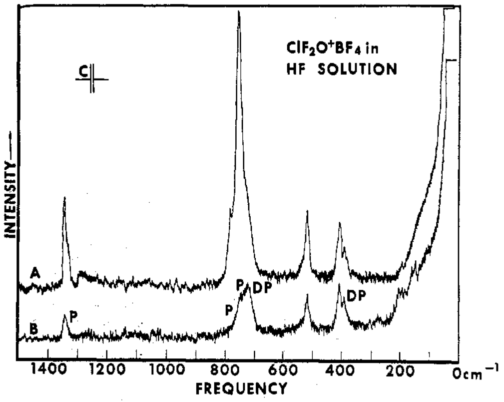

Figure 3.—Raman spectrum of $ClF_2O^+BF_4^-$ in HF solution: traces A and B, incident polarization perpendicular and parallel, respectively. C indicates spectral slit sidth.

The six remaining bands observed in the spectra of both $ClF_2O^+AsF_6^-$ and $ClF_2O^+BF_4^-$ complexes should be due to ClF_2O^+. A four-atom ion of the type ZXY_2, such as ClF_2O^+, could have C_{2v} or C_s symmetry. Distinction between symmetry C_{2v} and C_s should be possible by means of polarization measurements on the Raman bands. For symmetry C_{2v}, we would expect three polarized Raman bands, whereas for C_s, four of them should be polarized. The Raman spectrum of $ClF_2O^+BF_4^-$ in HF solution (Figure 3) shows that of the bands assigned to ClF_2O^+, three bands (1333, 741, and 512 cm^{-1}) are clearly polarized and one (710 cm^{-1}) is depolarized. It is difficult to determine the polarization state of the remaining two lines at 404 and 384 cm^{-1}, respectively. However, polarization measurements[4] for isoelectronic SOF_2, which has a Raman spectrum very similar to that of ClF_2O^+, indicate that the less intense lower frequency mode is weakly polarized, and, hence, should be assigned to $\nu_4(A')$. Intuitively, however, one might expect the $\nu_4(A')$ mode to result in a more intense Raman line than $\nu_6(A'')$. Unfortunately, Figure 3 does not allow a clear-cut distinction between the two possible assignments. Consequently, assignments for ClF_2O^+ were made by complete analogy with SOF_2, which was shown[17] to

---

[17] R. C. Ferguson, *J. Amer. Chem. Soc.*, **76**, 850 (1954).

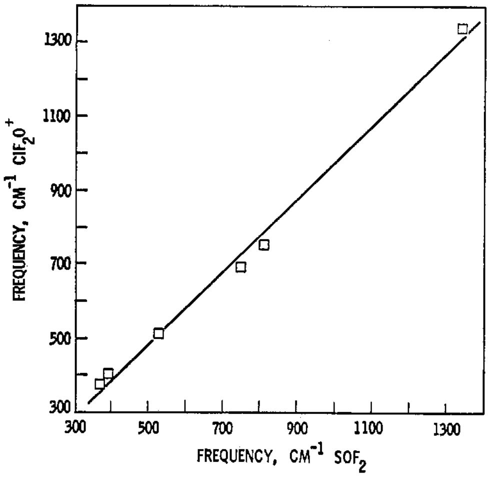

Figure 4.—Correlation between the vibrational frequencies of ClF_2O^+ and those of SF_2O.

have symmetry C_s. A plot of the vibrational frequencies of ClF_2O^+ against those of SOF_2 (see Figure 4) shows an approximately linear correlation. This linearity, together with relative band intensity considerations and the results from the force constant calculations (see below), supports the assignments given in Table I, although a possible reversal of the assignments of $\nu_4(A')$ and $\nu_6(A'')$ cannot entirely be excluded.

The spectra of both ClF_2O^+ and SOF_2 species show a frequency splitting of $\nu_1(A')$. Whereas for SOF_2 the splitting is due to Fermi resonance[4] between $\nu_1(A')$ and $\nu_2 + \nu_3(A')$, the splitting for ClF_2O^+ is due to the ^{35}Cl and ^{37}Cl isotopes. In ClF_2O^+, the combination band $\nu_2 + \nu_3$ has too low a frequency to account for the splitting of the band at about 1330 cm^{-1}. Furthermore, the frequency splitting of 12.5 cm^{-1}, observed under high resolution conditions, agrees well with the value of 12.6 cm^{-1} calculated for $^{35}ClF_2O^+$ and $^{37}ClF_2O^+$.

The vibrational spectrum obtained for the adduct $ClF_3O \cdot 1.22SbF_5$ clearly shows the bands characteristic for the ClF_2O^+ cation at 1331, 1319, 740, ~700, 510, 401, and 377 cm^{-1}. The remaining bands can be attributed to either SbF_6^- or polymeric anions such as $Sb_2F_{11}^-$.[18–20] Consequently, the formulation of the adduct as $ClF_2O^+SbF_6^-$ (containing some ClF_2O^+-$Sb_2F_{11}^-$) appears to be appropriate. Similarly, the 1:1 adduct[21] obtained in the reaction between ClF_3O and PtF_6 contains the ClF_2O^+ cation and, hence, is best described as $ClF_2O^+PtF_6^-$. The infrared spectrum[21] of $ClF_2O^+PtF_6^-$ shows, in the range 520–350 cm^{-1}, no absorptions due to the anion and, hence, proves that the three ClF_2O^+ deformation modes occur at about 500, 400, and 380 cm^{-1}.

Force Constants.—Two sets of force constants were computed for ClF_2O^+, assuming $\nu_6 > \nu_4$ (set I) and $\nu_4 > \nu_6$ (set II). Since SOF_2 and $SeOF_2$ are isoelectronic and have similar vibrational frequencies,[4] their force constants were reevaluated by the same method for comparison. The potential and kinetic energy metrics were computed with a machine method[22] using the geometries shown in Table II. The ClO and ClF bond lengths for ClF_2O^+ were estimated by comparison with similar molecules. The correlation noted by Robinson[23] between stretching frequencies and bond lengths predicts a value of 1.39 Å for the ClO bond length, which is only slightly shorter than that accepted here. The bond angles in ClF_2O^+ were estimated to be slightly larger than those in SOF_2, assuming that the mutual repulsion between the ligands will increase with decreasing ionic radius of the central atom.

TABLE II

BOND DISTANCES (Å) AND BOND ANGLES (DEG) ASSUMED FOR ClF_2O^+, SOF_2, AND $SeOF_2$

	$ClF_2O^{+\,a}$	$SOF_2^{\,b}$	$SeOF_2^{\,c}$
R(X=O)	1.41	1.412	1.576
r(X—F)	1.62	1.585	1.7255
β(O=X—F)	108	106.82	104.82
α(F—X—F)	93	92.82	92.22

[a] Estimated. [b] Reference 17. [c] I. C. Bowater, R. D. Brown, and F. R. Burden, *J. Mol. Spectrosc.*, **28**, 461 (1968).

TABLE III

VIBRATIONAL FORCE CONSTANTS OF ClF_2O^+, SOF_2, AND $SeOF_2$[a]

	ClF_2O^+			
	$\nu_6 > \nu_4$	$\nu_4 > \nu_6$	SOF_2	$SeOF_2$
f_R	11.21	11.20	10.84	7.87
f_r	3.44	3.44	4.03	3.57
f_β	1.72	1.65	1.73	1.28
f_α	1.59	1.78	1.52	1.04
$f_{\beta\beta}$	0.32	0.21	0.43	0.23
f_{rr}	0.25	0.39	0.42	0.37

[a] Stretching constants in mdyn/Å and deformation constants in mydn Å/radian^2.

The force constants were computed by trial and error with the aid of a computer, requiring exact fit between the observed and computed frequencies. The results are given in Table III where the force constants not shown were assumed to be zero. The values shown for the interaction constants, while not unique, were the simplest set that would give an exact fit. Since the force constants are underdetermined, a statistically meaningful uncertainty estimate cannot be made. Numerical experiments show that assuming different interaction constants, constrained to plausible values, resulted in valence force constants differing from those shown in Table III by less than 0.2. These uncertainties are estimates and are felt to be conservative. Of the two sets of force constants obtained for ClF_2O^+, set I ($\nu_6 > \nu_4$) is more plausible since it results in f_β ($\angle$O=Cl—F) being larger than f_α ($\angle$F—Cl—F). The good agreement between the force constants of the three species, ClF_2O^+ SOF_2, and $SeOF_2$, adds further credibility to our assignments for ClF_2O^+. Table IV shows the potential energy distribution for set I of ClF_2O^+. For set II, the results were similar, except for an appreciably larger contribution from $f_{\beta\beta}$ to ν_6. The potential energy distribution for SOF_2 and $SeOF_2$ was quite similar to that of ClF_2O^+. Only the

---

(18) J. K. Ruff, *Inorg. Chem.*, **5**, 1791 (1966).

(19) J. Weidlein and K. Dehnicke, *Z. Anorg. Allg. Chem.*, **348**, 278 (1966).

(20) F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc. A*, 2179 (1969).

(21) C. J. Schack, C. B. Lindahl, D. Pilipovich, and K. O. Christe, *Inorg. Chem.*, **11**, 2201 (1972).

(22) E. C. Curtis, *Spectrochim. Acta, Part A*, **27**, 1989 (1971).

(23) E. A. Robinson, *Can. J. Chem.*, **41**, 3021 (1963).

TABLE IV

POTENTIAL ENERGY DISTRIBUTION FOR ClF_2O^+

Assignment		Frequency, cm^{-1}	Potential energy distribution
A′	ν_1	1333	$0.97f_R$
	ν_2	731	$0.80f_r + 0.07f_\alpha + 0.06f_\beta + 0.06f_{rr}$
	ν_3	513	$0.76f_\beta + 0.14f_{\beta\beta} + 0.05f_r$
	ν_4	384	$0.91f_\alpha, + 0.08f_r$
A″	ν_5	695	$0.96f_r + 0.14f_\beta - 0.07f_{rr}$
	ν_6	404	$1.09f_\beta - 0.20f_{\beta\beta} + 0.11f_r$

more important terms are given in Table IV. These data show that the normal modes assigned to the observed vibrational frequencies are a good representation of the group vibrations described by the symmetry coordinates.

Force constants have previously been computed for both SOF_2 and $SeOF_2$. Our values for $SeOF_2$ are very similar to those reported by Paetzold.[24] For SOF_2, however, our results do not agree with those computed by Cotton and Horrocks.[25] The largest discrepancy was found for f_α[26] for which Cotton and Horrocks[25] report an abnormally high value of 3.47 mdyn Å/radian². This value appears much too high for this type of deformation vibration and cannot be explained by the slightly higher frequency value of 410 cm⁻¹ assumed for ν_4 by Cotton and Horrocks.[25]

The two constants of greatest interest are the two stretching force constants. Table V, showing a comparison of the Cl—O valence force constants of similar molecules and ions, reveals that f_R in ClF_2O^+ is larger by about 1.8 mdyn/Å than the largest value known for any other Cl=O containing compound. Whereas the formal positive charge on the central atom in ClF_2O^+ will certainly contribute to the high f_R value, it cannot account for it solely. Contributions from the resonance structures below could explain the high f_R value in ClF_2O^+. The following observation seems noteworthy. In ClF_4O^-, the Cl–O valence force constant value[2] is about the same as those in similar compounds, but the Cl–F valence force constant decreases dramatically. In ClF_2O^+, it is the ClO valence force constant which increases significantly, whereas the ClF valence force constant is within the usual range. This seems to indicate that the effective electronegativity of pentavalent chlorine is intermediate between those of oxygen and fluorine. Hence, in ClF_2O^+ the positive charge is partially located on the oxygen atom, whereas in ClF_4O^- the negative charge is mainly located on the fluorine ligands.

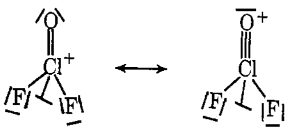

TABLE V

Cl–O VALENCE FORCE CONSTANTS AS A FUNCTION OF THE OXIDATION NUMBER AND FORMAL ELECTRICAL CHARGE OF THE CENTRAL ATOM

Species	f_R, mdyn/Å	Oxidation state of the central atom	Formal electrical charge on the central atom
ClF_2O^+	11.21	+V	Positive
ClO_3F[a]	9.41	+VII	
ClF_3O[b]	9.37	+V	
ClF_4O^-[c]	9.13	+V	Negative
ClO_2F[d]	9.07	+V	
ClO_2^+[e]	8.96	+V	Positive

[a] W. Sawodny, A. Fadini, and K. Ballein, *Spectrochim. Acta*, **21**, 995 (1965). [b] Reference 5. [c] Reference 2. [d] D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta*, **20**, 1763 (1964). [e] Reference 10.

The relatively high values obtained for both the ClO and ClF valence force constants in ClF_2O^+ indicate that the bonding in ClF_2O^+ is best described by a mainly covalent bond model employing sp³ hybridized orbitals of the chlorine atom for the two Cl–F bonds, the Cl–O σ bond, and the free electron pair. Bond models involving semiionic three-center, four electron p-p σ bonds[27-30] are not possible owing to the geometry of ClF_2O^+ (absence of linear F–Cl–F groups) and would result in a considerably lower value for the Cl–F valence force constants.

In summary, the ClF_3O·Lewis adducts investigated in this study are ionic and contain the ClF_2O^+ cation. The structure and bonding of this cation strongly resemble those of isoelectronic SOF_2. The close correlation between the two isoelectronic couples, ClF_2O^+–SOF_2 and ClF_4O^-–$XeOF_4$, respectively, demonstrates that the analogy between halogen fluorides and isoelectronic chalcogen or noble gas fluorides is likely to hold also for the oxyfluorides.

Acknowledgment.—The authors wish to express their gratitude to Dr. D. Pilipovich for his help in this work and to Dr. J. McTague of the Science Center of North American Rockwell and to Dr. D. Lawson of the Jet Propulsion Laboratory for the use of the Raman spectrophotometers. This work was supported by the Office of Naval Research, Power Branch, and by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under Contract AF49-(638)-1734.

---

(24) R. Paetzold, *Z. Chem.*, **4**, 272 (1964).

(25) F. A. Cotton and W. D. Horrocks, Jr., *Spectrochim. Acta*, **16**, 358 (1960).

(26) It should be pointed out that the definition of the angles α and β in our work and that of ref 23 is reversed. Furthermore, the value of f_α in ref 23 was normalized for distance to allow a better comparison.

(27) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

(28) R. J. Hach and R. E. Rundle, *J. Amer. Chem. Soc.*, **73**, 4321 (1951).

(29) R. E. Rundle, *ibid.*, **85**, 112 (1963).

(30) E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, *Advan. Inorg. Chem. Radiochem.*, **3**, 158 (1961).